NASA CR-152281

ULTRATHIN METALLIZED PBI PAPER

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DECEMBER 1978

(NASA-CR-152281) ULTRATHIN METALLIZED PBI PAPER Final Report (Celanese Research Co., Summit, N.J.) 48 p HC A03/MF A01 CSCL 07D

N79-25230

Unclas
G3/27 26239

Prepared under Contract No. NAS2-9526

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Summit, New Jersey 07901

for

AMES RESEARCH CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

FINAL REPORT

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by

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December, 1978

Contract NAS 2-9526

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ABSTRACT

A study to determine the feasibility of preparing ultrathin papers with a target weight of 3.5 g/m^2 from polybenzimidazole (PBI) fibrids was undertaken. PBI fibrids and porous mats therefrom were previously prepared under NASA contract NAS3-20040. The chemical and environmental resistance of PBI is excellent and the subject of numerous reports.

Small hand sheets of target weight were fabricated. They were light brown, low density materials with sufficient strength to be readily handleable. Characterization of these sheets included strength, fold endurance, thermal gravimetric analysis in air and nitrogen and photomicrographs.

Kimberly-Clark Corp. was supplied with two different batches of PBI fibrids. Differences in fabrication performance were noted. In neither case could target weight papers be prepared using conventional paper making techniques.

SUMMARY

The feasibility of preparing paper-like porous mats of non-flammable polybenzimidazole (PBI) was established under NASA contract NAS 3-20040. Extension of this technology to demonstrate the feasibility of producing an ultrathin paper with a target weight of 3.5 g/m^2 was the objective of this contract.

By suitable adjustment of operating parameters, fine PBI fibrids were made from which hand sheets were formed which met the target weight. Sheet density was about one third that of PBI polymer, thus a significant void structure is presumed to exist. Calendering of these 8×10^{-6}m thick sheets might be expected to densify them and further reduce their thickness, however this was not demonstrated. These thin light brown papers were readily handleable, could be creased without failure, had good fold endurance, and had tensile strengths in the range of 5.9-11.4 MPa(850-1650 psi).

Two pilot plant lots of PBI fibrids were submitted to Kimberly-Clark Corporation for their assessment of the fabricability of these samples into ultrathin papers. As the basis weight decreased below about 10 g/m^2, these papers did not have sufficient handling strength to be lifted off the forming screens. An integrated development effort addressing both the preparation and nature of the fibrids and paper-making technology would be required to successfully prepare lightweight PBI papers on a continuous basis.

RECOMMENDATIONS

Target weight PBI papers were made in the laboratory, despite low wet sheet strength, by allowing the PBI sheet to dry on the forming surface to develop strength and subsequently rewetting and stripping the sample. Since some batches of fibrids formed sheets more readily than did others, there appear to be differences in fibrid samples which have not yet been characterized. Because of this, an integrated development effort to examine the formation and nature of the fibrids and to improve paper making technology is recommended.

INTRODUCTION

Polybenzimidazole (PBI), or more properly poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole, is a non-flammable polymer and textile fiber which was developed at the Celanese Research Co. under Air Force and NASA contracts over the past fourteen years. Of the several thousand pounds of polymer made, most was converted into textile fibers and yarns for test and evaluation in Air Force and NASA applications requiring non-flammable woven, knitted, or braided flexible structures such as flight clothing and lanyards. Due to the outstanding thermal, physical, and chemical stability of PBI, it has been converted into hollow fibers and flat sheets for study as a reverse osmosis membrane. In preliminary testing of PBI mats as fuel cell or alkaline battery separators, excellent performance has been obtained.

While mats or papers have previously been made from finely chopped textile fiber, a more economical fibrid process was developed under NASA Contract NAS3-20040, and the fabrication of 0.2-0.3 mm thick porous mats for fuel cell and alkaline battery application was demonstrated.

Fibrids, which are short "fiber-like" materials with a somewhat irregular shape, are produced by coagulation of a polymer solution in a shear field which attenuates the polymer as it is being precipitated. The result is the formation of a hairy "fiber-like" material. Fibrids are ideal for paper making since their very irregularity leads to a strong degree of mechanical interlocking to provide strength without additional bonding steps.

In pursuing studies of fibrid preparation by precipitation of dimethylacetamide (DMAc) solutions of PBI, it was shown that very fine fibrids could be produced under conditions of high shear and slow coagulation rates with low viscosity dopes. These fibrids were thought to be suitable for producing very thin fine paper. Indeed, in December 1976 and January 1977, several small scouting samples were made which ranged from 3-10 g/m^2. These samples were the basis for the proposal which resulted in this contract.

OBJECTIVES AND STATEMENT OF WORK

This contract was divided into two phases. Phase I was to:

a. Apply established technology of PBI fibrid manufacture, taking into account the work conducted under NASA contract NAS 3-20040, to achieve fibrids of smaller dimensions by appropriate adjustments in fibrid manufacture.

b. Utilize the small diameter fibrids to fabricate thin papers. The papers to be fabricated using conventional suction techniques or appropriate modification thereof to provide PBI papers of 3.5 g/m^2 weight and thickness in the range of 2.5×10^{-6} m (0.1 mil).

c. Determine the physical properties of selected papers to provide data to assess project progress and to provide generalized data as to the strength of PBI paperlike materials. This included tensile strength, fold endurance, tear strength, thickness, weight, and thermal stability.

Phase II originally required selected samples of PBI paper be aluminized. However, after initiating work on Phase I, it was determined that techniques for metallizing PBI were available that would require little or no further development. For this reason, Phase II was redefined to demonstrate the suitability of the process for scale-up in commercial paper making equipment.

EXPERIMENTAL

A. PBI Polymer

Polybenzimidazole (PBI) is a polymer made by the melt condensation of 3,3',4,4'-tetraaminobiphyenyl (TAB) and diphenylisophthalate (DPIP). Typical polymer is a tan to light brown powder with an inherent viscosity of 0.7 to 0.8 dl/g (0.4g per 100 ml of 97% sulfuric acid). Besides acid, PBI is soluble in highly polar solvents such as dimethylformamide, dimethylacetamide, and dimethylsulfoxide. Dimethylacetamide (DMAc) containing 2% LiCl is the preferred solvent which has been used at Celanese to spin textile fibers from PBI.

Polymer solutions (dope) for this program were obtained from previously prepared and filtered fiber spinning dopes which were diluted with DMAc to lower solids and viscosity. Generally, a 4-5 poise dope was used, containing approximately 10% PBI. All dopes were crudely filtered after dilution through a layer of polypropylene felt to remove insolubles and trash. Extreme filtration associated with fiber spinning may not be necessary for fibrid preparation since the gel and particulate tolerances of the fibrid process are considerably greater.

B. Fibrids

Fibrids are produced by coagulating a polymer solution or dope in a shear field. Many types of mixing devices to do this have been described in the literature. However, a commercial spray nozzle produced by Spraying Systems Co. (Wheaton, Illinois, 60187) was used because these were readily available in a variety of sizes. The basic set up was a 1/4J internal mix round spray pneumatic atomizing nozzle, system No. 12A, consisting of fluid nozzle 2050 with air nozzle 73160. A PBI dope was fed to the fluid side of the nozzle with a typical fiber spinning dope gear pump (Zenith 5B, Zenith Products Co., W. Newton, Mass. 02165) and coagulant to the

air side of the nozzle with a high pressure piston pump (Teel 1P741, W.W. Grainger, Inc., Newark, N.J. 07102). A typical dope feed rate was 52 g/min (at 10% solids) with a pressure of about 50 psi. Coagulant flow rates were about 3500 g/min at a pressure of 225 psig. When water was used, the resultant 3552 g of slurry contained 5.2g polymer or about 0.15% solids with 1.3% DMAc. Slow coagulation with 70/30 DMAc/water rather than water alone produced very fine fibrids. These formed the strongest and densest papers. In such cases, the final slurry contained 70.3% DMAc.

In some cases, DMAc was removed from the fibrids prior to forming a paper. This was done by boiling the fibrid suspensions in water and filtering. Four boiling washes were generally used. Set fibrids were stored as slurries in water or in the original coagulation mixture of DMAc-water.

C Papers

Papers were produced by simply filtering the fibrid slurry. A weighed amount of slurry, generally 18-25g, was mixed with about 250 ml of water. This suspension was then filtered through a 12.5 cm coarse fritted glass filter funnel which had been overlayed with a sheet of Whatman #1 filter paper. A thin sheet was deposited on the filter paper. Washing of the paper was done on the filter by carefully pouring about 600 ml of warm water into the funnel without disturbing the sheet. This water was allowed to remain undisturbed for a few minutes in the funnel before the vacuum was turned on and the water filtered through the paper. After removal from the funnel, the sheet of filter paper containing the PBI sample was placed with the PBI side down on a sheet of polyethylene film. The sample was then covered with several additional sheets of filter paper and was restrained by a piece of 19 mm plywood and a 2 kg weight. After drying overnight, the filter paper was carefully removed by wetting it and peeling it from the PBI. Papers were then redried between sheets of filter paper which were kept flat with sheets of plywood and weights.

RESULTS AND DISCUSSION

A. Initial Scouting

Initial ultrathin papers were made using a fibrid sample made in November 1976 under conditions which were selected to produce very fine fibrids. This sample, 25536-37-6, was made using old PBI fiber spinning dope diluted with dimethylacetamide (DMAc) to 4-5 poise. The fibrid spray nozzle apparatus was fitted with an internal mix spray nozzle (#2050) with cap (#73160). Instead of water however, a 70% DMAc 30% water solution was used in an attemp to slow down the rate of polymer coagulation, thereby allowing the shear field in the mixing nozzle to attenuate the dope and thus to produce long thin fibrids. Coupled with a high coagulant pressure of 220 psig, a very fine fibrid resulted.

The first papers were formed directly from the slurry on filter paper in a 5.5 cm fritted glass funnel and were washed with hot water. As shown in Table I, these trials demonstrated the feasibility of producing ultrathin PBI papers in the target weight range of 3.5 g/m^2. These samples formed the basis for a proposal which ultimately resulted in this study.

The first fibrids made after receipt of contract NAS 2-9526, were direct extensions of the prior effort under contract NAS 3-20040 in preparing PBI mats for use as fuel cell and alkaline battery separators. Conditions were chosen to produce very fine fibrids. The finest dope nozzle with slow dope feed was used along with a large coagulant cap to produce high coagulant flows. Water was used as the coagulant. The relationship of flow rate to coagulant pressure for the two nozzle combinations used in this study is shown in Figure 1. These two curves are really the same within experimental error and show that the air cap size is the factor which controls flow rate.

TABLE I EARLY ULTRATHIN PBI PAPERS

Sample No.	Fibrid No.	Paper Weight (g)	Diameter (cm)	Thickness (10^{-6}m)	Thickness (mil)	Basis Weight (g/m^2)
25689-2	25536-37-6	0.0300	4.6	38	1.5	18
-6A	-37-6	0.0202	5.1	-	-	9.9
-6B	-37-6	0.0060	-	-	-	2.9[1]
-8	-37-6	0.0210	-	25	1.0	10.3[1]
-16C	25689-7-15A	0.0201	-	25	1.0	9.9[1]

[1] Calculated based on estimated diameter of 5.1 cm as -6A.

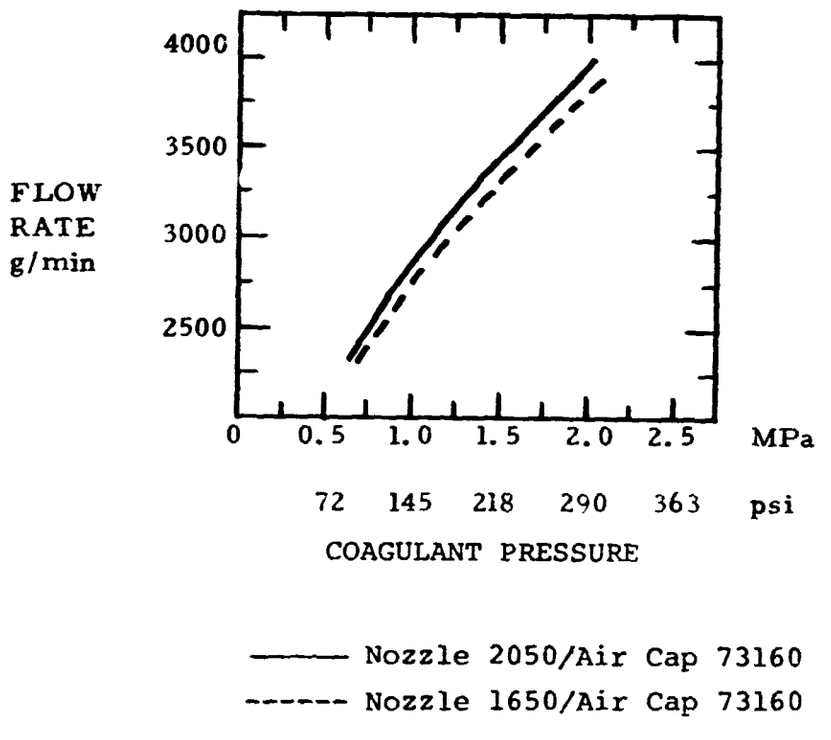


FIGURE 1 COAGULANT FLOW RATES FOR VARIOUS NOZZLE-AIR CAP COMBINATIONS

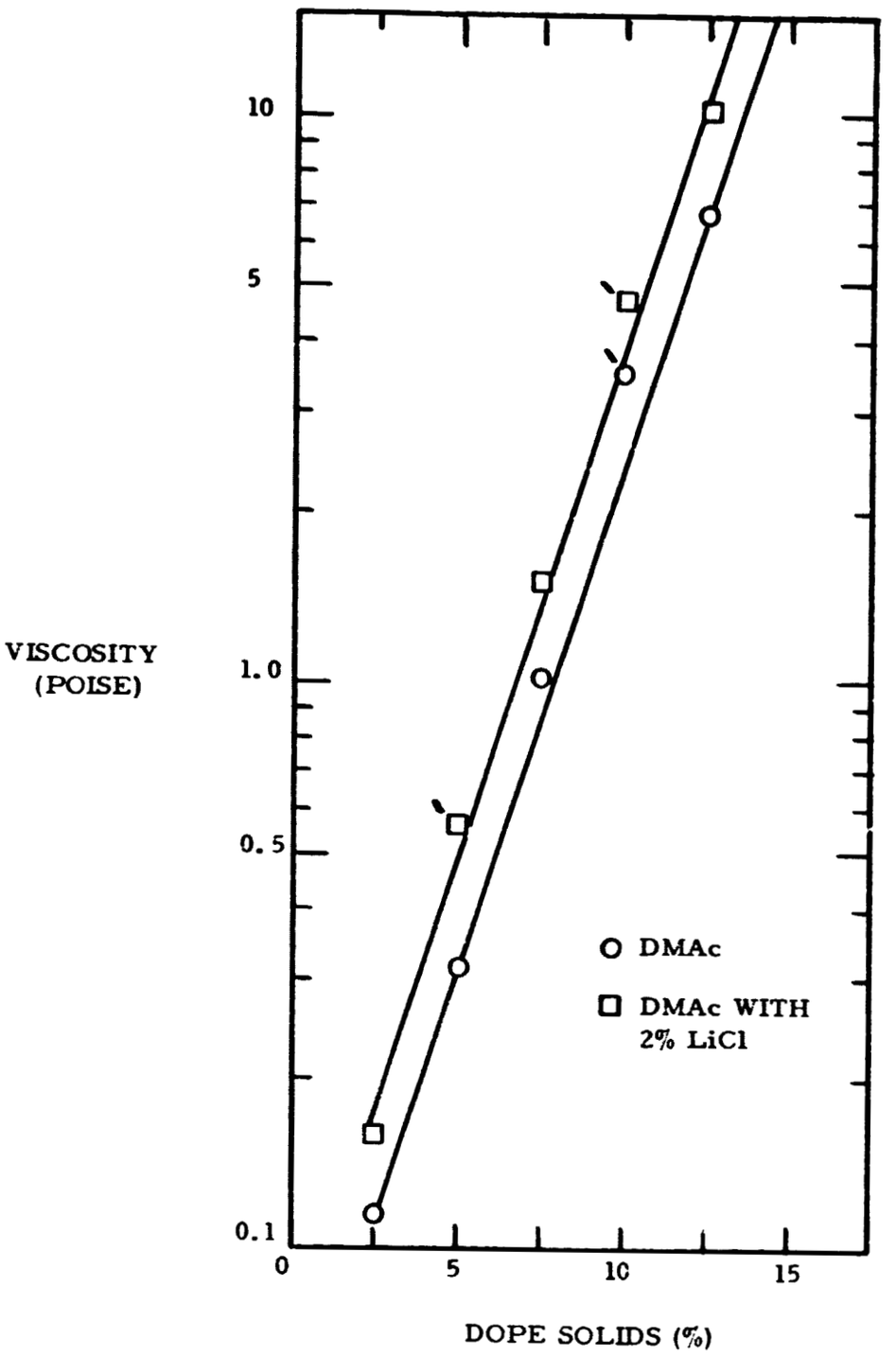
Besides the standard 4.3 poise (10% solids) dope generally used for production of coarser fibrids, one sample was diluted in half with DMAc to produce a 0.35 poise dope (5% solids). All fibrids were made with diluted fiber spinning dope which contains LiCl as a dope stability additive. At these low solids concentrations, it is not expected that the LiCl is necessarily required. Although its presence changes the solids-viscosity relationship, as shown in Figure 2, no effect of LiCl on fibrid formation was expected.

Fibrids were made at three different pressures with each of the two dopes. Coagulant pump size and power limits us to about 2.07 MPa (300 psi) maximum. Warm water was also used to increase the diffusion rate and thereby produce finer fibrids. Five gallon-sized samples were taken, however, due to foaming, only about half of the sample jar could be filled. Because of the low dope flow rate, the largest sample contained only 11 g of solids. Conditions for the preparation of these samples are shown in Table II.

These slurries were used to study paper formation. Forming the sheet was not difficult but removing it from the fabrication surface and drying it was. Very high shrinkage was encountered, just as had been found previously for thicker mats. This shrinkage either caused considerable wrinkling of the sheet or caused the sample to imbed itself in the screen or other filter surface upon which the paper was formed.

Shrinkage had been virtually eliminated in the case of fuel cell and battery mats by complete removal of the DMAc from the fibrids by washing in hot water. A further deswelling of the then solvent-free fibrids was accomplished via an azeotropic distillation of water from a toluene slurry. After filtration and air drying, the resulting fibrids could be resuspended in water and formed into mats or papers with little subsequent shrinkage.

It is reasonable to speculate that this effect is due to the several levels of hydration which occur in the polymer. First, is the normal moisture absorbed in PBI, about 13%, which will be present under most any circumstances. The wet fibrid, with a relatively loose structure, likely



Flagged points were obtained by dilution of sample. Other points represent a separate sample for each concentration.

FIGURE 2 DOPE VISCOSITY OF PBI IN DIMETHYLACETAMIDE WITH AND WITHOUT 2% LiCl

TABLE II FIBRID PREPARATIONS

Sample[1] No.	Dope			Water		
	Viscosity (Poise)	Pressure MPa (psi)	Flow Rate (g/min)	Temperature (°C)	Flow Rate (g/min)	Pressure MPa (psi)
25946-6-1	0.35	0.03 (4)	17.1	44	2390	0.79 (115)
-2	0.35	0.14 (20)	17.1	40	3905	2.07 (300)
-3	0.35	0.12 (18)	17.1	34	3785	2.07 (300)
-4	0.35	0.12 (18)	17.1	37	3240	1.45 (210)
-5	4.3	0.24 (35)	17.1	37	2395	0.83 (120)
-6	4.3	0.52 (75)	17.1	30	3890	2.07 (300)
-7	4.3	0.34 (50)	17.1	30	3040	1.31 (190)

[1] #1650 fluid nozzle, #73160 air cap.

holds a considerable amount of water between the polymer chains. Upon drying, the space occupied by the water collapses and thus leads to significant shrinkage. Finally, the fibrid as made is also swollen with solvent. As the solvent is removed, further shrinkage occurs. Shrinkages of 20%, as measured by a diameter change in round specimens, have been observed for thick mats made directly from the fibrid slurry. Washing with hot water to remove solvent has reduced shrinkage to 5-10% while azeotropically dewatering the fibrids allows preparation of mats with under 5% shrinkage. Each of these treatment steps tends to produce a softer, less dense, weaker structure as might be expected since solvent bonding is eliminated and mechanical interlock is diminished when shrinkage is not present to lock in the structure. Since one objective of this contract was to produce very lightweight papers, it was felt that maximum strength would be desirable. For this reason, the above scheme was generally not followed except to verify the previous conclusions.

During this period of trial with the samples shown in Table II, it was realized that an attempt must be made to reproduce the fibrids of sample 25536-37-6 from which the original papers were made. The most significant feature of this sample (25536-37-6) was that a mixture of DMAc-water (70-30) had been used as the coagulant rather than water in order to decrease the coagulation rate. Recognizing that this coagulant should produce a somewhat finer fibrid, a new trial was made. Two samples were produced, one as close a duplicate as possible to 25536-37-6, the other a bit coarser. Conditions used for making these materials are shown in Table III.

From these new slurries, successful thin 5.5 cm diameter papers were made on filter paper as had been done during the initial scouting trials. We then experimented with various paper making procedures. Eventually, after numerous trials, the procedure described in the experimental section was developed. The PBI sheet is formed on filter paper, rinsed with water to remove solvent, allowed to dry to develop handling strength, and finally moistened with water to soften the filter paper allowing it to be carefully peeled from the sample. As soon as successful samples were made, scale-up to 12.5 cm diameter sheets was done to provide samples large enough to obtain physical test data.

TABLE III FIBRIDS MADE IN 70/30 DMAc/WATER

Sample[1] No.	Dope		Coagulant		
	Pressure MPa (psi)	Flow Rate (g/min)	Temperature (°C)	Flow Rate (g/min)	Pressure MPa (psi)
25946-23-1	0.33 (48)	52.1	38	3160	1.24 (180)
-23-2*	0.39 (56)	52.1	39	3480	1.55 (225)

[1] #2050 fluid nozzle, #73160 air cap, 4.7 poise dope

* Duplicate of 25536-37-6

B. Sample Evaluation

The initial papers made from the above fibrid slurries (25946-23-1 and -2) are shown in Table IV. Each of these was produced as described above. Sample diameter can be used to calculate shrinkage, i.e. starting with a 12.5 cm wet sheet, if the dry sheet ends up as 11.6 cm, the shrinkage is 14%. Sample shrinkage was 11-29% for these samples, undoubtedly reflecting changes in restraint during drying. All of these samples were too heavy, being mostly in the 5-7 g/m^2 range. Thickness was measured with a TSI electronic micrometer which tended to compact the sample somewhat. In addition, typical samples were not uniform in thickness, therefore thickness values as reported are considered to have a low degree of accuracy. Nonetheless, using the measured thickness, apparent densities of 0.4-0.6 g/cm^3 were calculated. From these apparent densities, it was concluded that a considerable void structure must be present, since the density of PBI is 1.34 g/cm^3. This porous nature is noticeable in photomicrographs (Fig. 3 and 4).

To obtain physical properties on these papers, a 15 mm wide strip was cut with a Twing-Albert JDC Precision Sample Cutter through the most uniform section of the specimen. Breaking load was then obtained on a 25.4 mm gauge length at a 100% per minute strain rate. Only a single break was obtained from each sample. After testing, the thickness of the specimen in the break area was determined from which the tensile strength was calculated. Due to the aforementioned difficulties encountered in measuring the thickness, a more useful value as used in the fabric and paper industries is strip strength, g/cm. As shown in Table V, papers made with slurry-23-2 were generally twice as strong as those made with slurry-23-1, an expected result since the finer material (23-2) should have more fibrids per unit weight and thus have a greater amount of mechanical entanglement. Several of these samples have tensile strengths in the 14-20 MPa region (2000-3000 psi), surprisingly high numbers for these thin materials.

Folding endurance was measured on the material remaining from the 15 mm wide tensile strips with an M.I.T. Fold Endurance Tester (ASTM-D-2176). Sample conditioning was not done according to the standard method, the samples simply being conditioned in the ambient laboratory. Likewise, cooling of the specimen and head was not done.

TABLE IV EVALUATION OF ULTRATHIN PAPERS

Sample No.	Fibrid 25946-	Paper				
		Diameter (cm)	Weight (g)	Thickness (10^{-6})	Density (g/cm^3)	Basis Weight (g/m^2)
25946-25-1	23-1	-	0.0747	18	-	-
-2	23-1	11.6	0.0618	14	0.42	5.85
-3A	23-1	11.8	0.0580	13	0.41	5.26
-3B	23-1	11.6	0.0654	12	0.51	6.24
-27-1	23-1	11.2	0.0565	24	0.24	5.73
-25-4	23-2	11.1	0.0744	14	0.56	7.78
-5	23-2	11.8	0.0733	13	0.53	6.76
-27-2	23-2	11.0	0.0359	16	0.24	3.78
-3	23-2	11.5	0.0475	10	0.444	4.51
-4	23-2	10.5	0.0473	13	0.41	5.46
-5	23-2	-	-	17	-	-

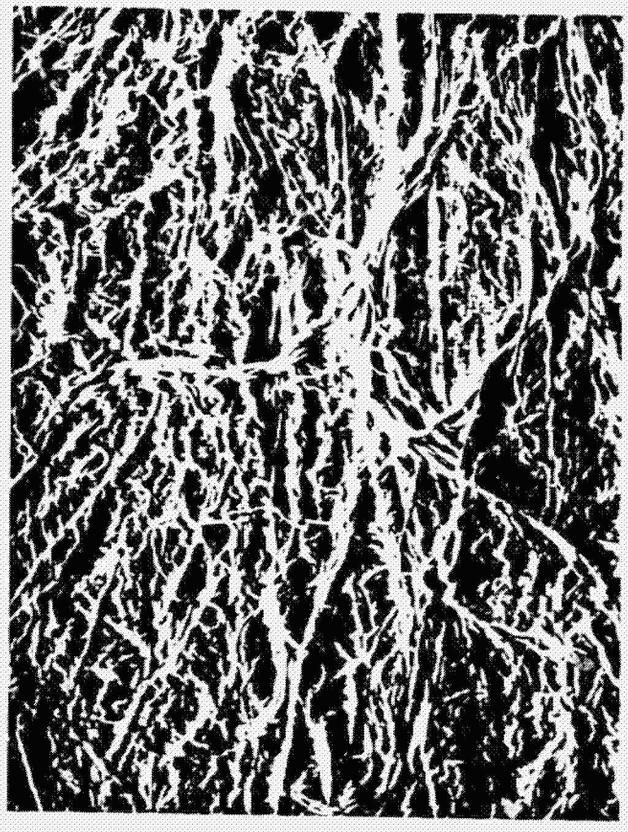
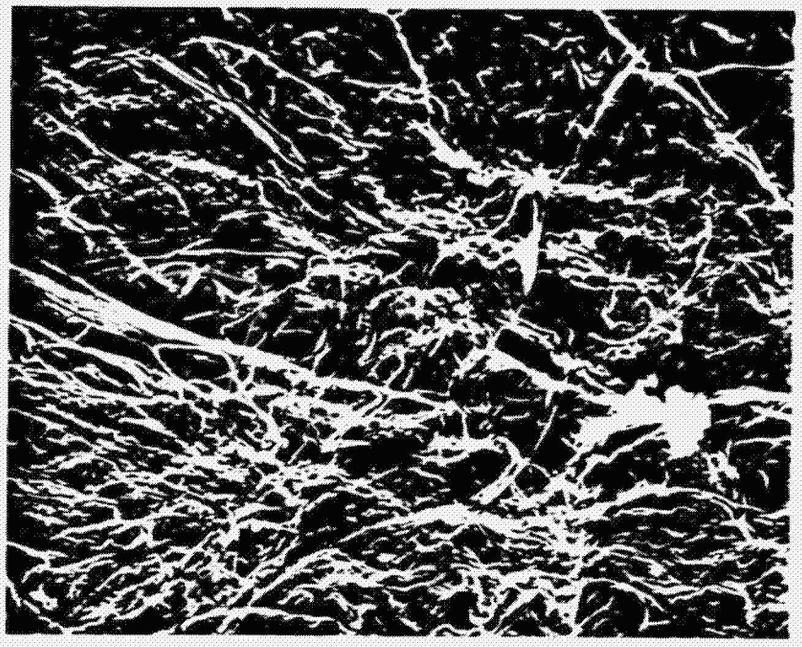
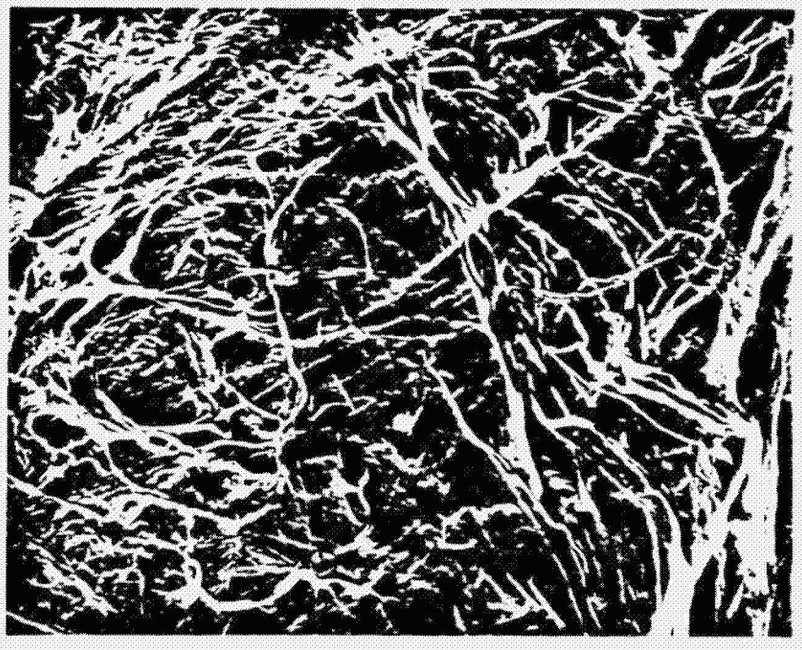


FIGURE 3 SEM OF PAPER 25946-44-6 (2000X)



A. Paper 25946-47-2



B. Paper 25946-47-3

FIGURE 4 SEM OF PAPER (2000X)

TABLE V STRENGTH AND FOLD ENDURANCE

Sample No.	Breaking[1] Load (g)	Strip Strength (g/cm)	Thickness (10^{-6}m)	Tensile Strength (MPa)	Tensile Strength (psi)	MIT Fold Endurance[3] (25g)	(50g)	(100g)	(250g)
25946-25-1*	78	52	30	1.70	247	878 34224	3 10		
-2*	98	65	13	4.93	715	14419 1971	7707		
-3A*	168	112	12	9.16	1330			2190	
-3B*	165	110	12	8.77	1270		196 373		
-27-1*	180	120	39	2.99	434		4240 3622	10	
-25-4+	430	287	14	19.8	2870			14539 17200	
-5+	420	280	12	23.7	3440			9958 31636	6883
-27-2+	62	41	8	5.27	764				
-3+	255	170	11	15.7	2280		10988	2438	
-4+	263	175	13	13.1	1900		8868 8060	327	
-5+	185	123	14	8.40	1220		4 6		

[1] Measured on 15mm wide strips, 25.4mm gauge length, 100%/min strain rate.

[2] As measured on the tested tensile strip.

[3] Cycles to failure on 15mm strip with loads shown ASTM D 2176.

* Paper made from Fibrid slurry #25946-23-1

\+ Paper made from Fibrid slurry #25946-23-2

The testing machine was modified to incorporate a pulley and weight arrangement whereby any pre-load could be imposed upon the sample by addition of weights. To experiment with the apparatus, several samples of graph and tracing paper were tested for tensile strength and fold endurance at different loads. While the test is quite variable and thus requires a large number of samples, it was found that a test load of 20-25% of the breaking load gave a 1000-2000 cycle to failure test. These conditions, then, were used, especially in testing a very limited number of PBI strips. As shown in Table V, the fold endurance of most of these PBI papers was good and generally much better than would be expected, based upon our tests with cellulose papers. Of course, the test is flaw sensitive, and thus the two or three samples which were tested give only a qualitative representation of the fold endurance. Otherwise similar papers, such as 25946-25-3A and B, did not give similar fold endurance results, possibly due to flaws. On the other hand, 25946-27-3 and 4, as well as 25946-25-4 and 5 gave reasonably comparable fold endurances as related to their strengths.

With a paper making technique established, three earlier fibrid samples were examined. A sufficient amount of the original slurry of 25536-37-6 remained to produce one sample. (This was the slurry from which the original papers shown in Table I were produced.) A paper was also made with 25689-7-15A, a water coagulated fibrid used in initial scouting (shown in Table I) and for comparison, another water coagulated sample, 25946-6-1 (shown in Table II). These papers turned out rather heavy, 11 g/m^2, but most surprising was the high density of 0.8 g/cm^3 found for the paper from fibrid -37-6. This is the highest density sample which has been made and also the strongest with a breaking load of 1040 g and a tensile strength of 43 MPa or 6200 psi. Fold endurance was found to be excellent even at loads approaching 70% of ultimate.

Sample No. 25689-7-15 also formed a sheet with excellent strength, surpassing the samples shown in Table V, although at a significantly higher basis weight. This also demonstrates a potential for the preparation of high strength sheets from samples which do not contain large quantities of solvent. The third sample, from 25946-6-1 was by far the poorest as had been expected. Due

to some breaks in the sample, density data were not calculated. Clearly as shown in Tables VI and VII, the old retain fibrid slurry, 25536-37-6, made with aqueous DMAc coagulant was the best material.

C. Target Weight Papers

Of the currently prepared samples, fibrid number 25946-23-2 had yielded sheets with the best properties. Therefore, successively lighter and lighter sheets were made from this sample until target weight was reached. As shown in Table VIII, samples 259-40-1 thru 4 demonstrate the reproducibility of formation of thick papers while successive samples decrease in weight until sample 13 with a weight of 3.25 g/m^2 is reached. All of these samples have densities of about 0.5 g/cm^3.

Two replicates of -13 were made, -41-1 and -2. Note that while these are weight replicates, 3.36 and 3.27 g/m^2, their thickness is significantly greater than the -40 series, consequently their density is much lower (0.33 g/cm^3). Table IX provides some explanation for this since the actual thickness of the tensile strips tested was found to be significantly greater than that shown in Table VIII where average values were shown. The values reported in Table IX show all three samples to be similar in thickness as indeed they are similar in breaking load and fold endurance. For this reason, -41-1 and -2 can be considered excellent replicates of -40-13. Excellent strengths and fold endurances were found for all of these samples.

Four additional papers were made at this time from fibrids which had been boiled with water in order to remove the DMAc. This was expected to produce a different degree of swelling of the fibrids, less shrinkage, a lower level of entanglement bonding, and no solvent bonding due to the lack of DMAc. Two different fibrid samples were used; 25946-7, which was a washed aliquot of 25946-6-1 (See Tables II, VI, VII), and 25946-39, which was a water washed aliquot of 25946-23-2 from which the rest of the -40 series was made (Tables VIII, IX). Data for these samples is shown in Tables X and XI. Notice that the papers in Table X have very low densities, ~0.2 g/cm^3, by comparison with papers

TABLE VI EVALUATION OF PAPERS FROM EARLIER FIBRIDS

Sample No.	Fibrid No.	Paper				
		Diameter (cm)	Weight (g)	Thickness (10^{-6}m)	Density (g/cm^3)	Basis Weight (g/m^2)
25946-28-1	25689-7-15A	10.8	0.196	23	0.49	11.1
-2	25946-6-1	-	-	13		
-3	25536-37-6	11.0	0.1107	14	0.82	11.6

TABLE VII STRENGTH AND FOLD ENDURANCE OF PAPERS FROM EARLIER FIBRIDS

Sample No.	Breaking[1] Load (g)	Strip Strength (g/cm)	Thickness (10^{-6}m)	Tensile Strength (MPa)	Tensile Strength (psi)	MIT Fold Endurance[3] (50g)	(250g)	(500g)
25946-28-1	905	603	22	27.3	3960		3324 6061	239
-2	163	109	12	9.11	1320	130		
-3	1040	693	16	43.3	6280		53451 57510	17281 329

[1] Measured on 15mm strips, 25.4mm gauge length, 100%/min strain rate.

[2] As measured on the tested tensile strip.

[3] Cycles to failure on 15mm strip with loads shown, ASTM D 2176

TABLE VIII PAPERS MADE FROM 25946-23-2 FIBRIDS

Sample No.	Paper Diameter (cm)	Weight (g)	Thickness (10^{-6}m)	Density (g/cm^3)	Basis Weight (g/m^2)
25946-40-1	12.0	0.0682	12	0.49	6.03
-2	12.0	0.0700	11	0.54	6.19
-3	12.0	0.0713	12	0.52	6.30
-4	11.9	0.0692	11	0.58	6.22
-6	11.9	0.0638	10	0.55	5.73
-7	11.7	0.0586	9	0.59	5.45
-8	12.1	0.0554	8	0.61	4.82
-9	12.1	0.0512	7	0.60	4.45
-10	12.0	0.0500	8	0.59	4.42
-11	12.0	0.0437	8	0.50	3.86
-12	11.8	0.0386	7	0.50	3.53
-13	11.9	0.0362	7	0.49	3.25
-41-1*	11.9	0.0060	10	0.32	3.36
-2*	10.4	0.0051	10	0.34	3.27

* Values shown were obtained on the tensile strip rather than on the entire sample.

TABLE IX STRENGTH AND FOLD ENDURANCE OF PAPERS MADE FOR 25946-23-2 FIBRIDS

Sample No.	Breaking[1] Load (g)	Strip Strength (g/cm)	Thickness[2] (10^{-6}m)	Tensile Strength (MPa)	Tensile Strength (psi)	MIT Fold Endurance[3] (25g)	(50g)	(100g)
25946-40-1	285	190	15	12.76	1852		19216 13138 10262	18854
-2	265	177	15	11.25	1632		8754 4262	368 5651
-6	200	133	15	8.72	1265		3629 643	205
-8	200	133	12	10.90	1111		310 480	1
-9	193	129	11	11.69	1695		926 310	1
-11	127	85	12	6.75	979	13077 327		
-12	125	83	10	7.86	1140	1699 9260	1 3	
-13	117	78	10	7.58	1099	7548 2803	1 4	
-41-1	97	65	10	6.10	885	22399 174	1 1	
-2	107	71	10	7.21	1046	6716 1126	1	

[1] Measured on 15mm strips, 25.4mm gauge length, 100%/min strain rate.

[2] As measured on the tested tensile strip.

[3] Cycles to failure on 15mm strip with load shown, ASTM D-2176.

TABLE X PAPERS MADE FROM WASHED FIBRIDS

Sample No.	Fibrid 25946-	Paper Diameter (cm)	Weight (g)	Thickness (10^{-6}m)	Density (g/cm)	Basis Weight (g/m^2)
25946-40-14	-7(1)	11.5	0.0663	31	0.21	6.38
-15	"	11.5	0.0859	34	0.24	8.27
-16(2)	-39(3)	12.0	0.0072	26	0.16	4.00
-17(2)	"	12.0	0.0091	20	0.26	5.06

[1] An aliquot of 25946-6-1, boiled with four changes of water to remove DMAc, and resuspended in water to original volume.

[2] Values shown were obtained on the tensile strip rather than on the entire sample.

[3] An aliquot of 25946-23-2, boiled with four changes of water to remove DMAc and resuspended in water to original volume.

TABLE XI PROPERTIES OF PAPERS MADE FROM WASHED FIBRIDS

Sample No.	Breaking[1] Load (g)	Strip Strength (g/cm)	Thickness[2] (10^{-6}m)	Tensile Strength (MPa)	Tensile Strength (psi)
25946-40-14	247	165	34	4.70	681
-15	155	103	38	2.67	387
-16	82	55	26	2.10	305
-17	155	103	20	5.12	743

[1] Measured on 15mm strips, 25.4mm gauge length, 100%/min strain rate.

[2] Measured on the tested tensile strip.

made from the original slurry, ~0.5g/cm^3. This situation was also observed with thick mats. Boiling to remove the residual DMAc from the fibrid seems to bulk the fibrid producing a softer, more open, low density structure. Strengths are lower than for comparable weight samples made from the original slurries containing DMAc. However, to provide a fair comparison, it is really necessary to compare the breaking loads at a given basis weight rather than tensile strength, which is adversely affected due to the thickness of the samples. Thus, we must compare samples -40-16 and -17, with their breaking loads and densities of 82g/4.00 g/m^2 (Tables X and XI), with samples -40-6, 8, 9, 11 with 200g/5.73 g/m^2, 200g/4.82 g/m^2, 193g/4.45 g/m^2, 127g/3.86 g/m^2 (Tables VIII and IX). Thus, these papers, made from washed fibrids really have between 50 and 75% of the strength of a similar paper made from the original DMAc slurry rather than the 33% to 50% observed when comparing tensile strengths. Both washed fibrid samples tested had similar strengths. To produce strong thin papers, fabrication from the original DMAc containing slurry remains the preferred route.

D. Physical Properties of Target Papers

Since sample 25946-40-13 met the target weight of less than 3.5g/m^2, two series of replicate samples were made to provide samples for testing. One set, 25946-43, formed on 12.5 cm filter paper yielded nine sheets of 11.7 to 12.0 cm diameter with basis weights of 3.08 to 3.59 g/m^2. These papers thus seem quite reproducible. The second series, 25946-44, was scaled up in size to 15 cm diameter. Seven sheets were made which exhibited a somewhat greater variability than did the previous series with diameters of 13.5-14.3 cm and basis weights of 3.32-4.35 g/m^2. These samples are described in Table XII.

Since it would be advantageous not to store or ship a very dilute fibrid slurry in DMAc, two samples were made to assess the possibility of handling a damp slurry rather than the original dilute solvent-containing fibrid slurry. Sample 25946-47-2 was made by first forming a damp sheet from 25946-23-2 fibrids by filtration and then reslurrying this damp mass in 250 ml of water. This new slurry was then formed into a sheet and dried in the conventional manner. Sample 25946-47-3 was processed in the

TABLE XII REPLICATE PAPERS OF 25946-40-13

Sample No.	Diameter (cm)	Weight (g)	Basis Weight (g/m^2)
25946-43-1	11.8	0.0393	3.59
-2	11.8	0.0337	3.08
-4	12.0	0.0379	3.35
-5	11.9	0.0383	3.44
-6	11.8	0.0367	3.36
-7	11.8	0.0373	3.41
-8	11.8	0.0392	3.58
-9	11.9	0.0387	3.48
-10	11.7	0.0379	3.53
-44-1	14.0	0.0511	3.32
-2	14.3	0.0570	3.55
-3	14.0	0.0633	4.11
-4	13.9	0.0660	4.35
-5	14.3	0.0545	3.39
-6	13.5	0.0498	3.48
-7	13.8	0.0501	3.35

same manner except that an amount of DMAc was added to the final slurry equal to that which would have been there had the sheet been made in the normal fashion. Thus, we compared two samples made in the standard manner directly from the initial slurry containing DMAc (-44-5, -44-6), a sample filtered and reslurried with water and DMAc (-44-3), and a sample filtered and reslurried with water only (47-2). Properties of these papers are shown in Table XIII.

All four samples are close to target weight. Densities and basis weights in Table XIII are shown as computed for the entire sample as well as calculated on the tensile strip. Since the same thickness was used for both calculations, the results agree closely. Both reslurried samples are significantly thicker than the others which leads to low densities. Compaction may remedy this, although it was not tried. The actual breaking load seems to be similar for all four samples as shown in Table XIV, thus strength does not seem to be impared by the lower density. The addition of DMAc to sample -47-3 did not improve its strength; in fact, it is less strong than -47-2 which contained no DMAc. Thus, even though a formed sheet is not compacted or dried, sufficient fibrid interlocking occurs so that upon reslurring, clumps remain which lead to more porous lower density sheets than the original. Based upon this data, for good properties, it seems necessary to avoid any fibrid compaction prior to sheet formation.

Analysis of these samples for their DMAc content by dissolving them in sulfuric acid followed by GC analysis showed the presence of little DMAc. Sample -44-5 contained 0.26%, -44-6 contained 0.19%, while sample 47-2 contained 0.28%. The fourth sample, -47-3 was lost. These values are surprisingly low and certainly don't differentiate between the washed fibrid sample -47-2 and the regular samples -44-5 and -6. These results are in line with what we would expect for extensively washed samples, thus our washing during mat formation may have been better than we thought although some DMAc evaporation may have taken place during the long period (weeks) that the samples were exposed to the air.

Scanning electron micrographs were obtained on samples 25946-44-6, -47-2, and 47-3. Examination of Figures 3 and 4 reveals that the low density reslurried papers -47-2 and -3 do look somewhat different than -44-6, appearing more

TABLE XIII COMPARISON OF STANDARD AND RESLURRIED PAPERS

Sample No.	Fibrid Treatment	Diameter (cm)	Weight (g)	Paper Thickness[2] (10-6m)	Density (g/cm3)	Basis Weight (g/m2)
25946-44-5	None	14.3	0.0545	8	0.42	3.39
-44-6	None	13.5	0.0498	8	0.46	3.48
-47-2	Filtered Reslurry H_2O	11.8	0.0429	15	0.26	3.92
-47-3	Filtered Reslurry H_2O Plus DMAc	12.2	0.0415	27	0.13	3.55

	Based on 15mm tensile strip				
	Length (cm)	Weight (g)	Thickness (10^{-6}m)	Density (g/cm3)	Basis Weight (g/m2)
-44-5	10.0	0.0053	8	0.44	3.53
	10.8	0.0057		0.44	3.52
-44-6	13.2	0.0068	8	0.45	3.43
-47-2	11.1	0.0063	15	0.25	3.78
	11.7	0.0071		0.27	4.04
-47-3	12.1	0.0069	27	0.14	3.80

[1] All samples made with fibrids 25946-23-2.

[2] Thickness measured on the tensile strip.

TABLE XIV PHYSICAL PROPERTIES OF STANDARD AND RESLURRIED PAPERS

Sample No.	Breaking[1] Load (g)	Strip Strength (g/cm)	Thickness (10^{-6}m)	Strength (MPa)	Strength (psi)	Air[2] Permeability (sec)	Tear[3] Strength (g)	MIT Fold[4] Endurance (cycle) (*)	MIT Fold[4] Endurance (cycle) (**)
25946-44-5	72	48	8	5.89	854	62	6	75	1
	96	64		7.85	1140			5	
-44-6	128	85	8	11.0	1598	1576	4	365	
	120	80		10.3	1500			502	
-47-2	124	83	15	5.44	789	400			115
	183	122		8.03	116				132
-47-3	112	75	27	2.75	399	67			6
	82	55		2.02	292				8

[1] Measured on 15mm strip, 25.4mm gauge length, 100% min strain rate.

[2] Air permeability as measured by Gurley method, "Resistance to Air Flow", ASTM D-726B. This is the time in seconds for a standard volume of air to pass through the sample; thus, low numbers are more porous or contain holes.

[3] Elmendorf tear, 200g weight ASTMD-689.

[4] Cycles to failure on 15mm strip with load shown ASTM D-2176.

* 25g load

** 50g load

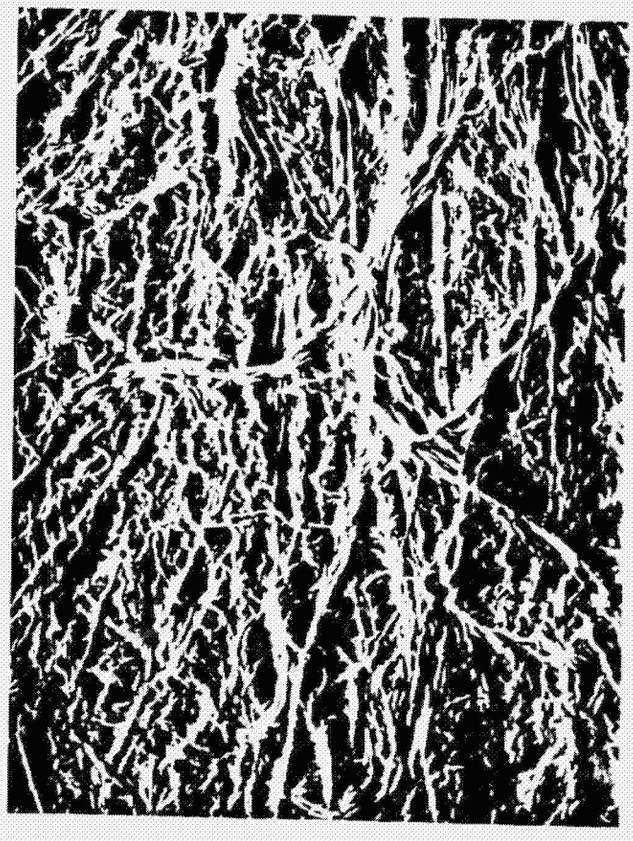
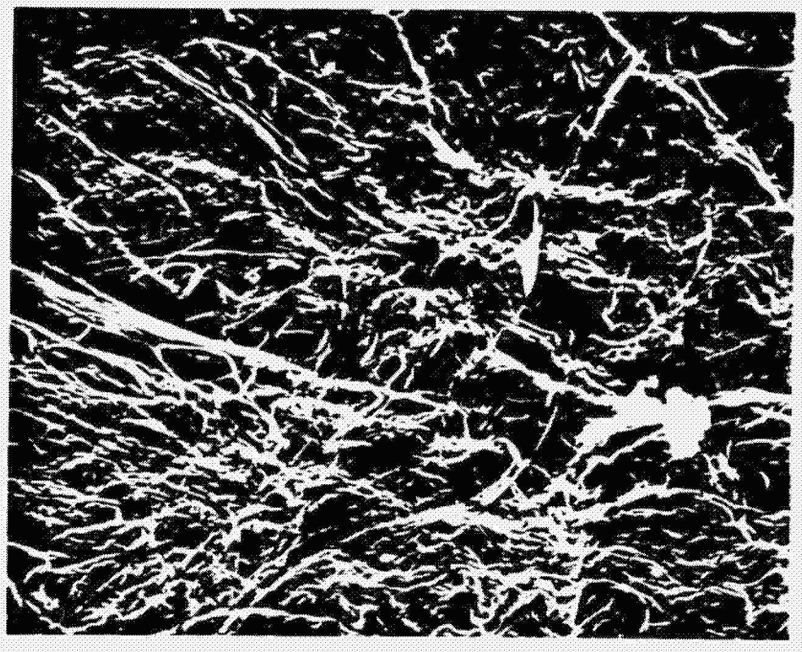
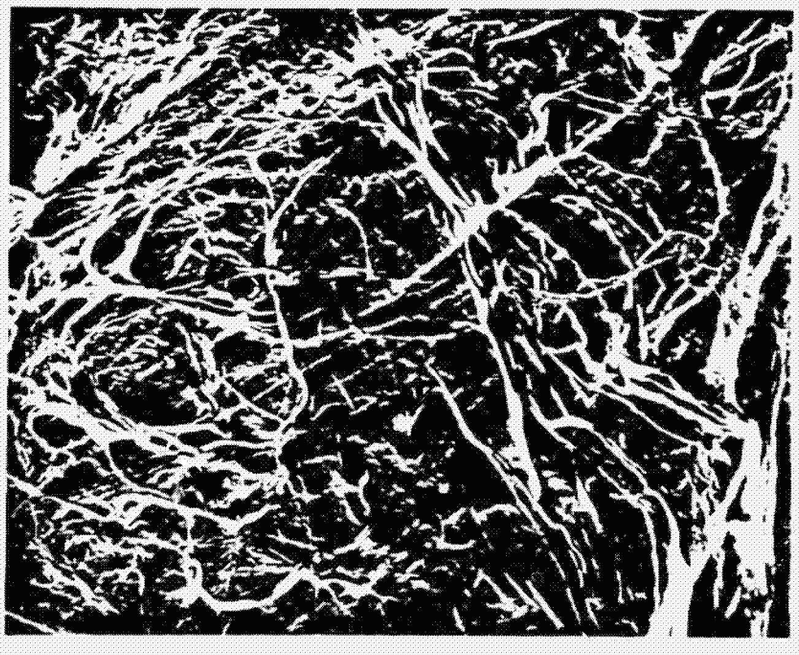


FIGURE 3 SEM OF PAPER 25946-44-6 (2000X)



A. Paper 25946-47-2



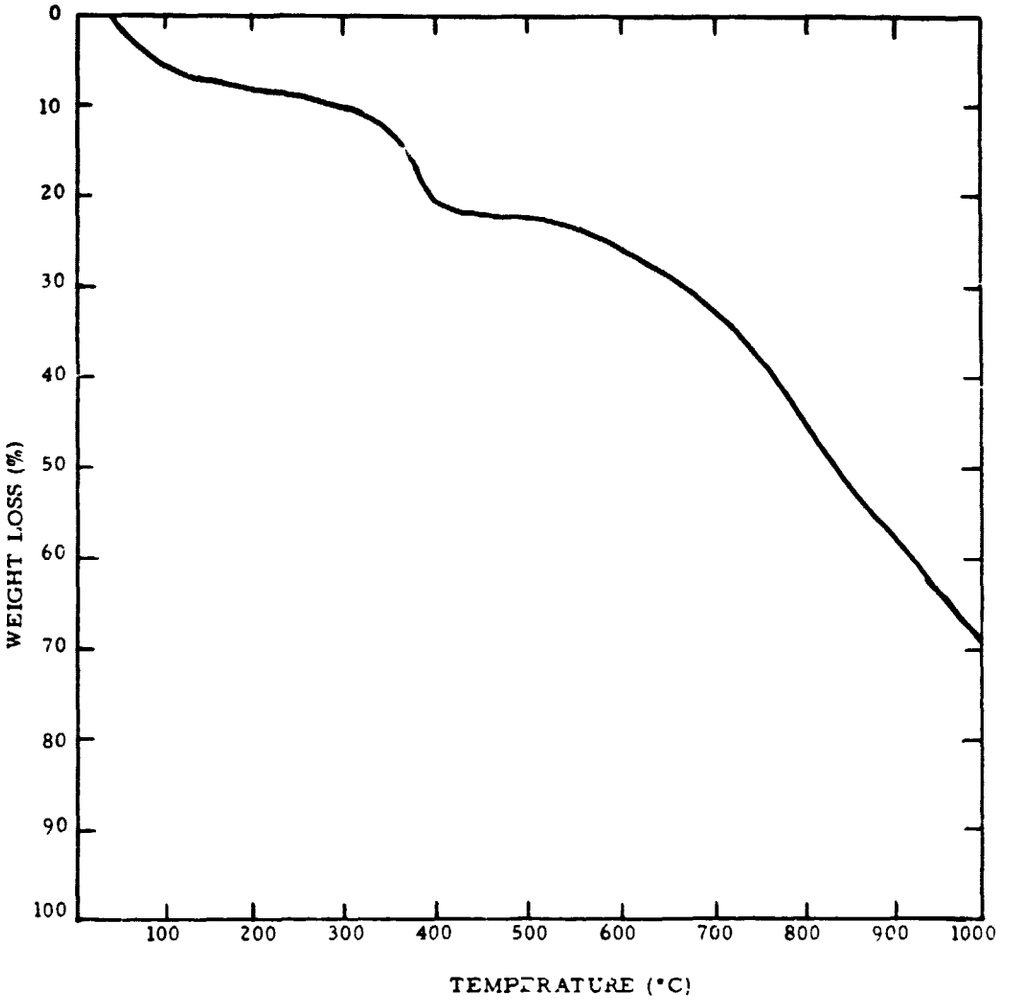
B. Paper 25946-47-3

FIGURE 4 SEM OF PAPER (2000X)

webbed and sheet like. While a picture of only one side is shown, no significant differences could be noted from one side to the other. Cross section pictures were attempted, however, it was difficult to cut a clean edge and the resulting qualities were poor.

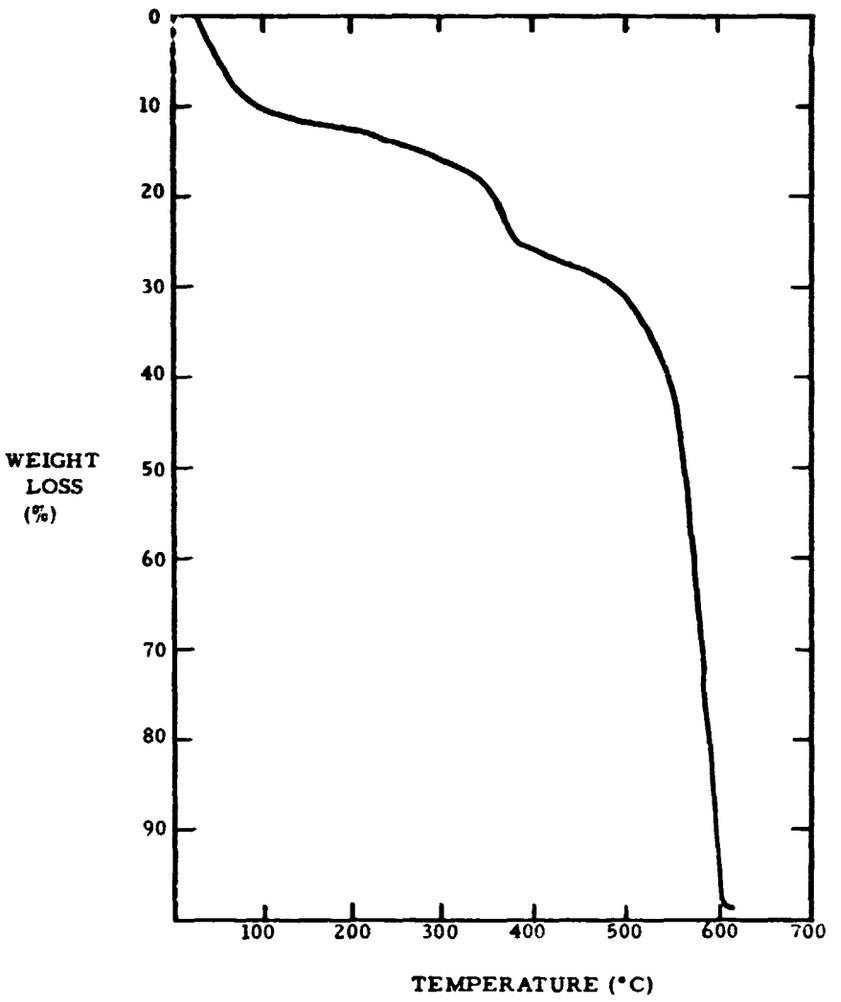
In addition to obtaining tensile strength and fold endurance on 15mm strips, we were able to determine air permeability by the Gurley procedure, ASTM D-726B and cut one sample from -44-5 and -6 for an Elmendorf Tear Propagation Test, ASTM D-689. The tear results for these samples are really below the capability of the instrument since the lightest beam weight is 200g. The air permeability tests show these samples to be relatively non-permeable but with large differences between them. A greater porosity of -47-2 and -47-3 as compared to -44-6 is shown which corresponds to some extent with the photomicrographs. Since any holes in the sample will also lead to low values, the very low value found for 25946-44-5 as compared with -44-6 could be due to defects.

Thermal Gravimetric Analysis (TGA) curves were obtained on paper 25946-44-6 in both air and nitrogen. These are shown in Figures 5 and 6. In both atmospheres, large amounts of material are driven off before polymer decomposition occurs. PBI adheres tenaciously to water and it is found normally to be still coming off above 250°C in the TGA apparatus. Since the moisture regain is about 13%, we expect the first 15% or so of weight loss to be water. DMAc is driven off thermally with very great difficulty which is why water washing is normally used to remove it from PBI. For this reason, it is assumed that the weight loss between 300-400°C was mostly from loss of DMAc. Thus we were surprised when the actual DMAc analysis received later showed so little. In air, the polymer disappears between 500 and 600°C, while in nitrogen, the polymer carbonizes and erodes away slowly at a constant rate. This behavior is typical for PBI polymer or fiber.



Specimen: 3.4 mg heated @ 15°C/Min

FIGURE 5 TGA OF PBI PAPER 25946-44-6 IN N_2



Specimen: 2.4mg heated @ 15°C/Min

FIGURE 6 TGA OF PBI PAPER 25946-44-6 IN AIR

E. Scale-up of Fibrid Process

In order to produce larger quantities of PBI fibrids for evaluation, a spray nozzle apparatus was set up in the pilot plant. Preparation of the coagulant mix was done by weighing the appropriate quantities of DMAc and deionized water into 55 gallon drums and thoroughly mixing them on a drum tumbler. This 70-30 DMAc-water mixture was then transferred to a gravity feed tank, from which it was pumped to the spray head by a high pressure piston pump.

A large batch of PBI dope was made up from reclaimed waste yarn. After filtration, this dope was diluted to the desired viscosity with DMAc by tumbling in a 55 gallon drum. A filter dressed with a coarse heavy paper was then attached to the drum and, with a few pounds of nitrogen pressure, the dope was filtered into clean 5-gallon containers. The filtered dope was then manually charged to a one gallon reservoir which fed the dope pump by gravity. The nozzles and pumps were the same as those used in the laboratory set-up. Fibrids were sprayed into a 50-gallon open top kettle from which they were drawn off into storage containers.

Two large batches of fine fibrids in 70-30 DMAc-water were made. The first was made with dope from resolutioned waste yarn. In preliminary trials, it was found that this dope behaved somewhat differently than did the earlier dopes used in the laboratory trials. A somewhat finer fibrid was produced at any given coagulation pressure. Analysis of the polymer samples showed that the new dope had a somewhat higher inherent viscosity (including weight) than did the old dope and thus, upon dilution to the same viscosity, would have a somewhat lower solids. A lower solids is believed to be the cause of the finer fibrids observed. Based upon laboratory trials, the coagulant pressure was reduced from 1.55MPa(225psi) as had been used for 25946-23-2 to 1.24 MPa(180psi) for this sample (26084-32). Five 55-gallon drums of fibrids were prepared, although not continuously due to mechanical problems. By settling and decantation, two drums were consolidated into one so that only four drums were shipped to Kimberly-Clark.

For the second large trial, a new batch of dope was prepared from a more recently produced polymer. The inherent viscosity of this polymer was 0.75, which is typical of a normal PBI. Dope was prepared as done routinely for fiber spinning; 24% solids, with 2% LiCl on the weight of DMAc (6% on weight of polymer). After being recycled through a filter to remove insolubles, the dope was transferred to a clean 55-gallon stainless steel drum. Additional DMAc was added to the drum to reduce the viscosity to the desired 5 poise (Brookfield RTV, Spindle No. 1, 10 rpm, 25°C). This 10.5% diluted dope was then refiltered as described above immediately prior to use to remove any possible dirt which could have entered the system.

A summary of these runs is shown in Table XV. The first batch, 26084-32, was stored in the same carbon steel drums in which the original DMAc had been received. After several months, it was noted that some rust could be seen in the drums. For this reason, when the second batch, 26374-12 was made, it was stored in stainless steel drums. With this dope, the original coagulant pressure of 1.55MPa(225psi) was used in an attempt to duplicate 25946-23-2. Due to operating problems, only 195 lbs. of slurry were made containing approximately 100g of solids. This amount was deemed sufficient for this study.

TABLE XV PILOT PLANT FIBRID PREPARATION

Sample[1] No.	Dope Pressure MPa	Dope Pressure (psi)	Dope Flow Rate (g/min)	Dope Temp (°C)	Coagulant Pressure MPa	Coagulant Pressure (psi)	Coagulant Flow Rate (g/min)	Coagulant Temp (°C)	Run Time (hr)	Run Quantity (Drums)
26084-32[2]	0.1	(18)	47.7	25	1.24	(180)	3200	30	5.5	5
26374-12[3]	0.4	(61)	47.7	20	1.55	(225)	3650	36	0.3	0.5

[1] Coagulant 70/30 DMAc/water by weight nozzle, #2050 fluid, #73160 cap.

[2] Dope prepared from resolutioned waste PBI yarn, filtered and diluted to 10.5% solids, viscosity, 4.7 poise @ 25°C.

[3] Dope prepared from fresh polymer, IV=0.75. Filtered and diluted to 10.5% solids, viscosity, 5.0 @ 25°C.

F. PBI Papers Produced by Kimberly-Clark

In order to assess the potential for the preparation of ultrathin PBI papers on a larger scale, the assistance of the Schweitzer Division of Kimberly-Clark Corporation was enlisted. In their initial work, they discovered the same things which had been observed in the laboratory trials, that the wet fibrid sheet had little handling strength and tended to adhere strongly to the forming screen. Of course, the thinner the paper, the worse the problem. After trying the second batch of fibrids, (26374-12) they found that it did not produce as strong or as thin a sheet as did the earlier batch (26084-32). Because of the multiplicity of shapes and sizes of individual particles found in fibrids, it is difficult to characterize them via microscopy. However, the difference in performance noted for the two large batches suggests a difference in fibrid size and or shape. Thus, in order to produce ultrathin papers by conventional paper making techniques, it will be necessary to improve reproducibility of the fibrid process and to control the fibrid morphology more closely. In this way, a more cohesive and stronger wet sheet would be expected.

Using conventional and state-of-the-art paper making equipment, Kimberly-Clark was unable to approach the target basis weight of $3.5 g/m^2$ with either sample supplied. Samples below $10 g/m^2$ were extremely difficult to handle as handsheets and would not be suitable for production on a continuous paper machine. Some samples prepared with 26084-32 and a basis weight of $20 g/m^2$ were delivered to us by Kimberly-Clark. These samples were judged to be of inferior quality and weak in strength. However, they represent the best handsheets which they were able to prepare from either fibrid sample.

The properties reported by Kimberly-Clark as well as properties measured by Celanese are shown in Table XVI. These samples were delivered to NASA-AMES.

TABLE XVI PROPERTIES OF KIMBERLY-CLARK HANDSHEETS

Sample[1] No.	Basis Weight (g/m^2)	Breaking[2] Load (g)	Strip Strength (g/cm)	Average[3] Thickness ($10^{-6}m$)	Tensile Strength (MPa)	Tensile Strength (psi)	MIT Fold Endurance[4] (Cycles)
26374-47-1	18.5	195	130	32	3.98	(578)	45
-2	17.5			34			
-3	18.4			34			
-4	17.8	205	137	31	4.32	(627)	52
-5	17.8			32			
-6	19.1			36			

[1] Received 6 sheets-assigned sample numbers as shown. Kimberly-Clark sample number 833-28-2. Prepared with 26084-32 fibrids. Properties reported were:

Basis weight - $20g/m^2$
Thickness - $25x10^{-6}m$ (1mil)
Strip strength - 134g/cm

[2] Measured on 15mm wide strips, 25.4min gauge length, 100%/min strain rate.

[3] Some areas on all sheets with thicknesses ranging from 40 to $60x10^{-6}m$ and folds, 60 to $80x10^{-6}m$.

[4] Cycles to failure on 15mm strip with 100g-load, ASTM D-2176.

CONCLUSIONS

Fine PBI fibrids can be produced by coagulating a PBI dimethylacetamide (DMAc) dope in a high shear field. From these fibrids, simple filtration can produce thin papers in the range of 3-4 g/m^2. Due to their low wet strength, a preferred laboratory technique has been developed whereby a sheet is made and allowed to dry on filter paper. Subsequently, the filter paper is rewetted and carefully peeled from the sample.

Denser but thinner papers can be produced from fibrids formed in DMAc water rather than water alone. Attempts to remove DMAc prior to sheet fabrication produced thicker lower density samples with a somewhat lower strength. Strip strengths of 50-80 g/cm were obtained. Fold endurance of these samples was excellent. Photomicrographs show the surface of the papers to be rough with visible pores. Sample duplicability on a laboratory scale has been demonstrated. Some laboratory handsheets have been sent to NASA-AMES for evaluation.

The laboratory method for making fibrids was scaled up and the fibrids so produced used by Kimberly-Clark Corporation in an attempt to demonstrate the feasibility of making ultrathin PBI papers by conventional paper-making technology.

Scale-up at Kimberly-Clark using conventional paper-making technology and equipment was unsuccessful primarily because the fibrids were of such size and shape that they produced sheets of lower wet strength than had previous samples. This, coupled with the tedious handling required, prevented them from producing lighter weight sheets than $10g/m^2$. Further development and characterization of both fibrid and paper-making technology will be required to successfully produce an ultrathin light weight PBI paper on commercial paper-making equipment.